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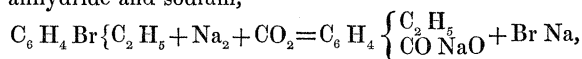
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plane geometry, but already very prominently in solid geometry; viz. we have here the difficulty as to the form of the equations of a curve in space, or (to speak more accurately) as to the expression by means of equations of the twofold relation between the coordinates of a point of such curve. The notion in question is that of a  $k$ -fold relation,—as distinguished from any system of equations (or onefold relations) serving for the expression of it,—and giving rise to the problem how to express such relation by means of a system of equations (or onefold relations). Applying to the case of solid geometry my conclusion in the general theory, it may be mentioned that I regard the twofold relation of a curve in space as being completely and precisely expressed by means of a system of equations ( $P=0, Q=0, \dots T=0$ ), when no one of the functions  $P, Q, \dots T$ , as a linear function, with constant or variable *integral* coefficients, of the others of them, and when *every surface whatever* which passes through the curve has its equation expressible in the form  $U=AP+BQ+\dots+KT$ , with constant or variable integral coefficients,  $A, B \dots K$ . It is hardly necessary to remark that all the functions and coefficients are taken to be rational functions of the coordinates, and that the word *integral* has reference to the coordinates.

IV. "On the Action of Bromine upon Ethylbenzol." By T. E. THORPE, Ph.D. Communicated by H. E. ROSCOE, Ph.D. Received November 11, 1869.

In the course of an investigation upon ethylbenzoic acid which Prof. Kekulé and I recently published in conjunction, we had occasion to prepare a quantity of monobromomethylbenzol,  $C_6H_4Br\{C_2H_5$ . Our object in this research was to prove experimentally the identity of the ethylbenzoic acid made synthetically by acting upon the monobromomethylbenzol by means of carbonic anhydride and sodium,

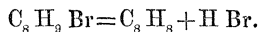


with the acid subsequently obtained by Fittig by oxidizing diethylbenzol,  $C_6H_4\left\{ \begin{array}{l} C_2H_5 \\ C_2H_5 \end{array} \right.$ , by means of nitric acid.

In the preparation of the bromide for the purposes of our experiments, we followed the direction given by Fittig and König, by whom this substance was first described. Bromine was added drop by drop to well-cooled ethylbenzol in the proportion of 1 mol. bromine to 1 mol. ethylbenzol, and the mixture was allowed to stand one or two days before distillation. The action of bromine upon ethylbenzol is extremely energetic, each drop of the bromine disappears almost immediately on coming in contact with the hydrocarbon, the mixture, unless carefully cooled, becomes very hot, and large quantities of hydrobromic acid are evolved. It is easy to perceive when the proper point in the substitution is reached, since after the addition of the theoretical quantity of bromine in order to form  $C_6H_4Br\{C_2H_5$ ,

the succeeding drops of bromine disappear with far less rapidity, a fact which evidently indicates that the substitution of the first atom of bromine is more easily effected than that of the second. After standing for about forty-eight hours, the liquid was shaken with a dilute solution of caustic soda, and then repeatedly washed with water, dried over calcium chloride, and submitted to fractional distillation.

The liquid commenced to boil at about 145°, and a comparatively large quantity passed over between 150° and 160°; a still larger fraction distilled over between 170° and 180°; but the greater portion came over between 180° and 190°, after which the temperature rapidly rose, and the residue in the flask became nearly solid, owing to the formation of a mixture of metastyrol and styrolbromide. Throughout the process of distillation large quantities of hydrobromic acid were evolved, and the portion boiling between 150° and 160° was found by the characteristic bromine reaction to consist mainly of styrol,



An analysis of the portion boiling between 180°–190° showed it to contain very nearly the theoretical amount of bromine calculated for



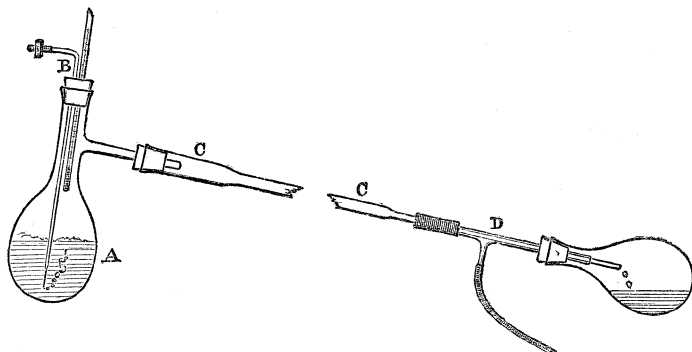
0.9742 grm. substance gave 0.9510 grm. silver bromide, and 0.0082 grm. silver

	Found.	Calculated.
Bromine . . . . .	42.1 %.	43.2 %.

This compound is very unstable; on renewed distillation it invariably commences to boil at about 140°, and unless the distillation is very rapidly conducted, a large proportion is transformed into styrol and hydrobromic acid. So easily is this decomposition effected, that on exposing 4 or 5 grms. of the liquid in a sealed tube to a temperature of about 200° for a few minutes, it is almost entirely converted into metastyrol, and on opening the tube torrents of hydrobromic acid are evolved. The formation of styrol may, however, be almost entirely avoided by conducting the distillation in a partial vacuum; and for this purpose the water-pump of Bunsen may be very conveniently applied. The accompanying figure shows the disposition of the apparatus employed for this purpose; as it may hereafter be found useful in operations of a like nature, the following description of its arrangement may not be superfluous:—The apparatus may easily be adapted to the process of fractional distillation *in vacuo*; by a slight modification it is possible to change the receiver without disturbing the partial vacuum in the remaining parts of the apparatus.

A represents the flask from which the liquid is distilled; it is fitted with a good cork pierced with two holes, into one of which fits a thermometer, and into the other a piece of thermometer tubing (B), one end of which nearly reaches to the bottom of the flask, and is drawn out into a fine capillary tube; to the other end a screw-clamp is fixed by means of a short piece of caoutchouc tubing. The object of this capillary tube is to

deliver a minute stream of air-bubbles, and thus to prevent the violent "bumping" which almost invariably occurs during ebullition *in vacuo*; the supply of air may be regulated at will by increasing or diminishing the



pressure of the screw-clamp on the caoutchouc tubing. This little device succeeds admirably; it is due to my friend Mr. W. Dittmar, who has already applied it in the distillation of sulphuric acid: so rapidly and effectually does the "water-pump" of Bunsen exhaust, that the minute amount of air passing through the liquid, and serving to maintain it in regular ebullition, is without appreciable effect upon the manometer. The flask is attached, as represented in the figure, to a long tube C, made preferably of thin glass, so as to allow the condensation and cooling to take place as rapidly as possible: over the end of the condenser slides a short length of wider glass tubing, which is fastened air-tight on to the condenser by an inch or two of caoutchouc tubing; the other end fits into a caoutchouc cork adapted to the receivers; on this short piece of wider tubing another piece of glass tubing is fixed at right angles, in order to connect the entire apparatus with the caoutchouc tubing leading to the "water-pump." The mode of using the apparatus hardly requires description; it will be self-evident to anyone familiar to the working of the Bunsen pump.

Distilled in a partial vacuum (about 0.5 m.) in the apparatus above described, the bromide boiled nearly constantly at 148°–152°, and left scarcely any residue of styrolbromide or metastyrol. The bromide thus obtained is a heavy colourless liquid, possessing the characteristic penetrating odour peculiar to all the aromatic substitution products in which the substitution has occurred in the lateral group; its vapour is extremely irritating, and excites a copious flow of tears when incautiously inhaled. When heated with solution of ammonia or potash in alcohol, it gives up its bromine with the greatest facility.

The monobromomethylbenzol,  $C_6H_4Br\{C_2H_5\}$ , described by Fittig, is a colourless aromatic-smelling liquid, possessing the sp. gr. 1.34, boiling constantly at 199° C., and capable of being distilled without decomposition. It may be boiled or heated in sealed tubes for any length of time with al-

coholic solution of potash or ammonia without giving up the least trace of bromine. It is evident, therefore, that the two bromides, although prepared under circumstances apparently exactly similar, are not identical. In all probability the bromide we obtained is identical with that recently prepared by Berthelot by acting upon boiling ethylbenzol with the vapour of bromine. To this compound the formula  $C_6H_5\{C_2H_4Br$  is assigned; it cannot be distilled without a considerable portion undergoing decomposition into styrol and hydrobromic acid, and loses easily its bromine by double decomposition.

It remained now to discover the cause of the variation in the position of the bromine atom. In the preparation of the two products the conditions were apparently identical; why, then, should the substitution have occurred in the phenyl group in the bromide obtained by Fittig, and in the ethyl group in our own? The cause of the difference was soon found to reside in the bromine employed. The bromine used by Fittig doubtless contained iodine. By digesting a few grains of the bromine employed in our experiments with water and granulated zinc, and, on the complete disappearance of all colour, filtering the solution, adding a small quantity of chlorine-water, and then shaking the mixture with a few drops of benzol, the absence of even a trace of iodine was shown by the benzol remaining perfectly colourless. By adding about 0.5% iodine to the bromine before allowing it to act upon the ethylbenzol, I easily succeeded in obtaining monobromethylbenzol with the properties described by Fittig. It distilled constantly without decomposition at  $203^\circ C.$ , and completely resisted the action of boiling alcoholic potash. A similar series of comparative experiments on cymol obtained from camphor was attended with like results. We have thus a ready method of effecting at will the kind of substitution required without the employment of heat, the presence or absence of iodine determines the position of the substituting bromine; in the one case substitution occurs in the phenyl group, in the other in the lateral group. The bromine obtained by Berthelot is described as boiling between  $200^\circ$  and  $210^\circ$ , whilst the bromide which I obtained distilled at  $190^\circ$ . I am disposed, however, to consider the higher number to be a nearer approximation to the truth. The difference observed in my case is probably due to the fact that in distilling the substance I operated on a larger scale than did Berthelot, and kept the liquid exposed to the influence of the high temperature for a comparatively longer time, thus working under conditions more favourable to the production of styrol and hydrobromic acid, the formation of which would necessarily tend to lower the boiling-point.

Nearly seven years ago Dr. Hugo Müller drew attention to the remarkable effect of iodine in facilitating the action of chlorine upon organic compounds. He showed that many substances which were acted upon with great difficulty by chlorine alone, and some of them only with the aid of direct sunlight, yield chlorine products with great ease when acted upon by chlorine in the presence of iodine. He failed, however, to point out

any difference in the *kind* of substitution effected by the halogen in the presence or absence of iodine.

Beilstein also has recently shown that the action upon toluol varies materially with the conditions under which the experiment is performed. When a stream of chlorine is passed through carefully cooled toluol, chlor-toluol,  $C_6H_4Cl\{CH_3$ , only is formed; this body is characterized by a high degree of stability, resisting completely the action of potassium cyanide, potassium sulphide, and silver-salts. On the other hand, if the toluol is previously heated, or if, through the energy of the action, its temperature be allowed to rise, the relative position of the substituting chlorine atom is essentially changed, and under these circumstances chlorbenzyl,  $C_6H_5\{CH_2Cl$ , is found to be the main product of the reaction: this substance differs from the isomeric chlortoluol by the facility with which it yields up its chlorine by double decomposition. But if a small quantity of iodine be added to the hydrocarbon before treatment with chlorine, chlortoluol only is produced, no matter whether the chlorine acts upon boiling or upon cold toluol.

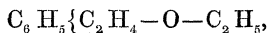
To the bromide obtained by the action of bromine free from iodine on cold ethylbenzol I assign the formula  $C_6H_5\{C_2H_4Br$ , on the assumption that it is identical with that prepared by Berthelot. From the ease with which the compound yielded its bromine to alcoholic ammonia, I was induced to attempt the preparation of the corresponding amines. A quantity of the bromide was sealed up in wide glass tubes with about four times its volume of absolute alcohol saturated with ammoniacal gas, and the mixture exposed to a temperature of  $100^\circ C$ . for about three hours. When all action had apparently ended, the tubes were reopened and the liquid portion drained from the bulky precipitate of ammonium bromide. On treating the liquid with water, a light mobile agreeably melling liquid separated out; this was washed, dried by means of calcium chloride, and distilled; by far the greater portion boiled at  $185^\circ$ – $187^\circ C$ . This liquid was found to be free from nitrogen and bromine, and yielded on analysis the following numbers:—

I. 0.1552 grm. substance gave 0.4540 grm. carbonic anhydride and 0.1333 grm. water.

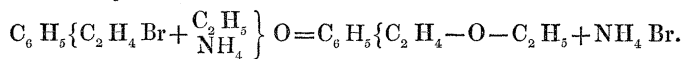
II. 0.2011 grm. substance gave 0.5896 grm. carbonic anhydride and 0.1078 grm. water.

	Calculated.		Found.	
			I.	II.
$C_{10}$ .....	120	80.00	79.79	79.98
$H_{14}$ .....	14	9.36	9.53	9.44
O .....	16	—	—	—

The constitution of this compound may be expressed by the formula

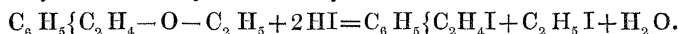


and its formation from the bromide by the action of ammonium alcoholate may be thus represented :—



For this substance I propose the name styrolylethyl ether. It is a colourless, mobile, fragrant-smelling liquid, boiling constantly at  $187^\circ$ , of specific gravity 0.9310 at  $21^\circ.9$ , slightly soluble in water, and burning with a strongly luminous flame.

When heated for a few hours with a concentrated solution of hydriodic acid in a sealed tube to about  $120^\circ$ , it was completely decomposed, and on distilling the liquid from a water-bath, a quantity of ethyl iodide, boiling at  $73^\circ\text{--}75^\circ$ , and easily recognizable by its characteristic alliaceous odour, distilled over; the presence of the alcohol rest in the new ether was thus demonstrated. The remainder of the liquid, containing the greater portion of the hydriodic acid and possibly the alcohol or its corresponding iodide, was treated with dilute caustic soda, when a heavy oily liquid separated out. This liquid was repeatedly washed with water and dried over calcium chloride. On distilling it, the greater portion of the liquid boiled between  $300^\circ$  and  $310^\circ$ , but with evident decomposition, iodine being evolved. The compound in all probability was the iodide corresponding to the bromide originally taken, already described by Berthelot.



The very small quantity of substance at my disposal prevented me from more accurately investigating the nature of this reaction, or the properties of the iodine compound formed.

I next sought to obtain the alcohol,  $\text{C}_6\text{H}_5\{\text{C}_2\text{H}_5\text{O}$ , already described by Berthelot as a colourless liquid of an agreeable aromatic odour, heavier than water, and boiling at about  $225^\circ$ . I attempted to prepare the acetate, intending to decompose the compound with caustic potash. Fifty grms. of the bromide diluted with double its volume of absolute alcohol were heated with about 40 grms. potassium acetate to  $100^\circ$  in a flask placed in a water-bath. The liquid was then filtered from the mass of potassium bromide, and again sealed up in tubes with a further addition of acetate, and heated to  $120^\circ\text{--}130^\circ$  for an hour or two. On cooling, the tubes were reopened and the contents treated with water, and the non-miscible portion separated and dried over calcium chloride. On standing over the calcium chloride, a crystalline precipitate was slowly formed, which was afterwards proved to be the compound of ethyl acetate and calcium chloride. On submitting the dehydrated liquid to distillation, a further quantity of ethyl acetate came over at  $72^\circ\text{--}74^\circ$ . The next fraction, boiling between  $140^\circ$  and  $150^\circ$ , was found to consist chiefly of styrol; the quantity, however, was so small that in all probability it was not a product of the reaction, but existed already formed in the bromide used for the experiment. The next and main fraction of the distillate came over between  $180^\circ$  and  $190^\circ$ , and on repeated rectification a constant boiling-point of  $185^\circ\text{--}186^\circ$  was obtained.

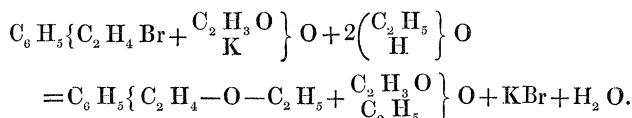
This substance, from its characteristic aromatic odour and from the following analyses, was identified as the styrolyl-ether already described.

0.2523 grm. substance gave 0.7358 grm. carbonic anhydride and 0.2119 water.

0.1993 grm. substance gave 0.5829 grm. carbonic anhydride and 0.1666 grm. water.

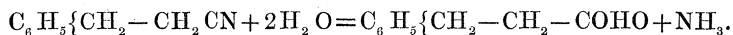
Calculated.		Found.	
		I.	II.
C <sub>10</sub> . . . . .	120      80.00	79.54	79.75
H <sub>14</sub> . . . . .	14      9.36	9.33	9.30
O . . . . .	16		

The simultaneous production of this body and of the ethyl acetate may be thus represented :—



The remainder of the distillate consisted principally of the acetic ether,  $\text{C}_6\text{H}_5\{\text{C}_2\text{H}_4-\text{O}-\text{C}_2\text{H}_3\text{O}\}$ . This body is a sweet-smelling liquid, possessing the characteristic fragrant odour of the acetic ethers and boiling at  $217^\circ$ – $220^\circ$ . The quantity produced, however, was so small as to preclude further investigation, or any attempt to prepare the alcohol.

Fittig has recently obtained phenylpropionic acid (hydrocinnamic acid),  $\text{C}_6\text{H}_5\{\text{CH}_2-\text{CH}_2-\text{COHO}\}$ , by acting upon chlorinated ethylbenzol by means of potassium cyanide and treating the resultant cyanide with potash.

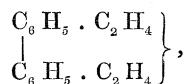


I have attempted to repeat this reaction with the bromide obtained by treating ethylbenzol with bromine free from iodine, but without success, although the experiment has been frequently made under the exact conditions described by Fittig. So easily, according to Fittig, is the transformation effected, that this chemist has recommended the reaction as affording the best method of obtaining phenylpropionic acid. I am unable to discover any reason for the discrepancy in the results of our observations. It is certainly very remarkable that the reaction should occur in the case of the chloride and not in that of the bromide.

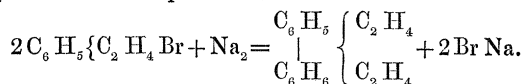
The experiments which led to the discovery of the above method of effecting the substitution of hydrogen in the phenyl or in the lateral group at will had for their object the preparation by synthesis of ethylbenzoic acid from the bromide,  $\text{C}_6\text{H}_4\text{Br}\{\text{C}_2\text{H}_5\}$ . It therefore became interesting to trace the reaction which occurs on submitting the new bromide to a similar treatment. A small quantity (about 7 grms.) of the bromide was mixed with about five times its volume of anhydrous ether, and a large excess of sodium cut into slices as thin as possible added, and a slow continuous



current of carbonic anhydride sent through the mixture. Not the slightest reaction was perceptible in the cold. The sodium remained perfectly metallic-looking, even after the expiration of twenty-four hours. On gently heating the liquid for a few minutes, a vigorous reaction at once set in; the mass became suddenly very hot, and gave off abundant fumes of hydrobromic acid and a small quantity of a thick oily liquid boiling at a high temperature, and possessing the character of the distyrol,yl,



described by Berthelot was produced,



The Society then adjourned over the Christmas Recess to Thursday, January 6th, 1870.

*January 6, 1870.*

Lieut.-General Sir EDWARD SABINE, K.C.B., President, in the Chair.

The Presents received were laid on the Table, and thanks ordered for them, as follows:—

Transactions.

- Birmingham :—Institution of Mechanical Engineers. Proceedings, 1868, 28, 29 July. Leeds Meeting, Part 3, Nov. 5; 1869, April 29. 8vo. *Birmingham*. The Institution.
- Cadiz :—Observatorio de Marina de la Ciudad de San Fernando. Almanaque Nautico para 1871. 8vo. *Cadiz*, 1869. The Observatory.
- Cherbourg :—Société Impériale des Sciences Naturelles. Mémoires. Tome XIII. 8vo. *Paris* 1868. The Society.
- Coimbra :—Observatorio da Universidade. Ephemeris Astronomicas para o anno de 1871. 8vo. *Coimbra* 1869. The Observatory.
- Danzig :—Naturforschende Gesellschaft. Schriften, neue Folge. Band II. Heft II. 8vo. *Danzig* 1869. Two copies (one with Photographs). The Society.
- Habana :—Colegio de Belen. Observaciones Magneticas y Meteorológicas. Año Meteorológico de 30 de Noviembre de 1867, a 30 de Noviembre de 1868. 8vo. *Habana* 1869. The College.
- London :—British Museum. Hand-List of Genera and Species of Birds, by G. R. Gray. Part I. 8vo. *London* 1869. Catalogue of the Specimens of *Dermoptera Saltatoria*, by F. Walker. Part 2. 8vo. *London* 1869. Guides to the First and Second Vase Rooms. 12mo. *London*